Investigation of the Potential of Some Plant Extracts to Inhibit the Corrosion of Duplex Stainless Steels in Acidic Media

J. H. Potgieter*[1], P.A. Olubambi[2] and N.P. Thanjekwayo[3]

[1]School of Research, Enterprise and Innovation, Manchester Metropolitan University, All Saints, Oxford Road, Manchester, M1 5GD, UK

[2]Department of Chemical and Metallurgical Engineering, Tshwane University of Technology, Private Bag X680, Pretoria, South Africa

[3]DST/NRF Centre of Excellence in Strong Materials, School of Chemical and Metallurgical Engineering, University of the Witwatersrand, Private Bag X3, Wits, 2050, Johannesburg, South Africa

*h. potgeiter@mmu.ac.uk

***Abstract*- The inhibitive effect of some natural organic compounds on the corrosion behaviour of duplex stainless steel was investigated. Inhibitors studied include natural honey and natural oils from various plant extracts. The honey was obtained from two sources, namely the blue gum tree (honey BG) and honey from orange blossoms (honey OB), while the oils consisted of rosemary, jojoba, eucalyptus, and mugwort oils. The inhibitory effects were studied on two different types of duplex stainless, namely steels 2205 and 2507, in 1 M hydrochloric acid and 1 M sulphuric acid solutions, using a potentiodynamic polarization method and varying concentrations of inhibitors (2.5, 5.0 and 10.0 g of inhibitors per litre of acid). Mugwort oil was found to be the best and effective inhibitor in hydrochloric acid media on both types of duplex stainless steels, while honey BG and honey OB showed good inhibitive effects in a 1 M sulphuric acid solution for 2205 and 2507 respectively. Inhibition was found to increase with increasing concentration of honey and the oils.**

Keywords- Corrosion; DSS; Plant Extracts; Hydrochloric Acid; Sulphuric Acid

I. INTRODUCTION

The overall cost and environmental implications of various problems associated with corrosion in many industries, have led to several efforts been adopted for reducing the risk of metals to corrosion. One of the most practical methods for protection against excessive dissolution of the metal by corrosion is the use of inhibitors. When small concentrations of corrosion inhibitors are added to corrosive media, they either decrease or prevent the reaction of the metal with the media.[1,2] An inhibitor hinders corrosion reactions either by reducing the probability of corrosion occurrence or by reducing the rate of attack or both.[2,3] Inorganic substances such as phosphates, chromates, dichromate and arsenates are often used in process industry applications as inhibitors to decrease the corrosion of various types of alloys, mostly mild and low carbon steels. However, they suffer a major disadvantage because of their high toxicity, and as such their use has come under severe criticism.[4,5] These toxicity effects have resulted in renewed interest in organic substances as anticorrosion agents, because they are more eco-friendly and mostly harmless.[1,6] Organic substances containing polar functional groups with oxygen, nitrogen and/or sulphur atoms in a conjugate system are of particular interest and have been reported to exhibit good corrosion inhibiting properties.[2,5,7,8]

Due to the toxic nature of inorganic-based compounds and their associated high costs, efforts have been focused on the use of the plant extracts as potential agents to reduce corrosion in various typical industrial solutions. Inhibitors from plant extracts are renewable resources, readily available, acceptable and environmentally friendly.[2,6,9] The corrosion inhibition activity in many of these plant extracts is ascribed to the presence of heterocyclic constituents like alkaloids, flavonoids, etc. contained in them. It has been reported previously that the presence of tannins, cellulose and polycyclic compounds normally enhances the film formation over the metal surface, thus preventing corrosion.[2]

The chemical composition and structure of essential oils from the plants extracts make them attractive to consider as potential corrosion inhibitors. The constituents of some of these oils are known to have an inhibitive action, and their extracts could thus exert a retarding action on dissolution of different metals. Natural honey has been found to act as an inhibitor for the corrosion of C-steel A 106[10-12], and can be used in petroleum fields to reduce the corrosion rate of steel pipelines. Benabdellah *et al.*[13] found that Mugwort oil (Artemisia oil) can act as a good inhibitor for the corrosion of steel in an acid medium and as a cathodic inhibitor by modifying the hydrogen reduction mechanism. Bouyanzer and Hammouti[14] also reported that the corrosion rate of steel was significantly reduced in the presence of jojoba, thus indicating that jojoba oil acted as a corrosion inhibitor.

Despite a number of studies that reported the use of plant extracts as corrosion inhibitors, these studies concentrated mostly on non-ferrous metals and mild/low-alloyed steels. Investigations on stainless steels were inhibitors are seldom used, are few and far between. Amongst the few exceptions is the use of Khillah extracts as inhibitor for acid corrosion of SX 316 steel.[2,5,8] The possibility of using natural occurring extracts as inhibitors for duplex stainless steel, which has wider industrial applications in aggressive environments than other alloys, has not been given any consideration yet. Although duplex and super duplex steels offer superior advantages over the austenitic and ferritic grades, Bendall[15] observed that they are no exception to corrosion problems, as they have a limit to their acid corrosion resistance and safe temperature for use in chloride and acidic chloride environments. Normally, duplex stainless steels are used on their own in fairly severe corrosive conditions. However, there is no theoretical reason why corrosion inhibitors cannot be used with stainless steels, and effective corrosion inhibition

has the potential to increase the use of stainless steels under conditions where they would not normally be employed. Alternatively it could result in lower maintenance and replacement costs in applications where stainless steels are used and eventually suffer corrosion failure.

It was therefore decided to evaluate the potential use of selected African plant extracts as corrosion inhibitors in hydrochloric and sulphuric acid for duplex stainless steel. As most previous literature reports concentrated on more commonly used steels and alloys, it was expected that this investigation could achieve both the goals of making a contribution to the knowledge and appreciation of our naturally occurring resources, as well as establishing their suitability for preventing the corrosion of duplex stainless steels. This investigation not only has the potential to enhance the use of natural products as corrosion inhibitors, but also to increase the application range of duplex stainless steels.

II. MATERIALS AND EXPERIMENTAL PROCEDURE

The approach adopted in this study was to use potentiodynamic polarisation scans to determine typical corrosion characteristics that can give an indication of the materials susceptibility to corrode, and then add varying concentrations of the different plant extracts to the corrosive solutions to determine their effect on the process. The parameters of interest included the corrosion current, from which the corrosion rate could be calculated, and the corrosion potential gave an indication of the tendency of the alloys to passivate spontaneously in the corrosive environment or undergo active corrosion. The smaller the corrosion current, the lower is the corrosion rate, and the more noble (less electronegative) the corrosion potential, the more thermodynamically stable is the particular alloy in that environment and the lower will be its tendency to corrode. Any plant extract that could have a beneficial effect on either of these parameters, offers potential for further extensive evaluation as a corrosion inhibitor under these conditions.

A. Materials

The duplex stainless steels used for this study were obtained in a plate form. Their nominal chemical compositions are shown in Table 1. The inhibitors comprise four different types of essential oils, including rosemary, eucalyptus, jojoba and mugwort (i.e. Artemisia) and two types of honey (Honey from orange blossoms [honey OB] and honey from blue gum trees [honey BG]).

TABLE 1 CHEMICAL COMPOSITION (WT %) OF SAF 2205 AND 2507 DSS USED FOR STUDY

	Percentage Composition (%)										
Sample	**Cr**	**Ni**	**Mo**	**Si**	**Mn**	**N**	**Cu**	**S**	**P**	**C**	**Fe**
2205 DSS	21.8	5.7	2.9	0.4	1.43	0.15	0.15	0.002	0.023	0.02	Bal
2507 DSS	24.85	7	3.79	0.3	0.4	0.243	0.31	5E-04	0.015	0.015	Bal

B. Experimental Methods

1) Microstructural Observation

The stainless steel plates were cut into pieces of 1 cm^2. The samples were hot mounted in embedded epoxy resin, ground with silicon carbide paper from 240 down to 1000 grade, and polished with several grades of diamond pastes to obtain a mirror-like surface. The polished surfaces were cleansed in distilled water, degreased with acetone, and electro-etched with oxalic acids to reveal the details of their microstructures. Microstructural observations were carried out using an Axiotech microscope (Carl Zeiss AG, Oberkochen, Germany) equipped with an AxioCam MRc digital camera.

2) Electrochemical Tests

Electrochemical measurements were carried out in a conventional three electrode cylindrical glass cell, with a stainless steel counter electrode and a silver/silver chloride, 3 M KCl, reference electrode. Working electrodes were prepared by attaching an insulated copper wire to one face of the sample using an aluminium conducting tape, and cold mounted in resin. The surfaces of the samples were wet ground with silicon carbide papers from 240 down to 600 grit. They were washed with distilled water, degreased with acetone and dried in air. As is the usual practice, the edges of the mounted alloys were blanked off by using a lacquer to prevent crevice corrosion.

Corrosion behaviour of the samples was investigated in 1 M hydrochloric acid and 1 M sulphuric acid solutions and with different concentrations of inhibitors (2.5, 5.0 and 10.0 g of inhibitor per litre of acid). Electrochemical measurements were made at room temperature (25 ± 2^0C) with an Autolab potentiostat (PGSTAT20 computer controlled) using the General Purpose, Electrochemical Software (GPES) version 4.9. The software determined the corrosion potential (E_{corr}), corrosion current (I_{corr}) and corrosion current density (i_{corr}) from the polarization experiments, and calculated the corrosion rates. Before potentiodynamic polarization, working electrodes were immersed in the electrolytes and allowed to stabilize at the open-circuit potential (OCP). Polarization curves were measured at a scan rate of 0.2 mV/s starting from -500 mV to 1250 mV. Most of the tests were carried out in triplicate. The reproducibility and repeatability were good as there were no significant differences between the repeats.

III. RESULTS AND DISCUSSION

A. Microstructural Observation

The typical micrographs of the microstructures of the two as-received duplex stainless are shown in Fig. 1. The gray region in the micrographs corresponds to the ferritic phase (α) while the white region corresponds to the austenitic phase (γ). The grain sizes of 2507 were observed to be coarser than those of 2205. This could be attributed of the heat treatment process on the samples and probably the increased nickel contents of the type 2507.

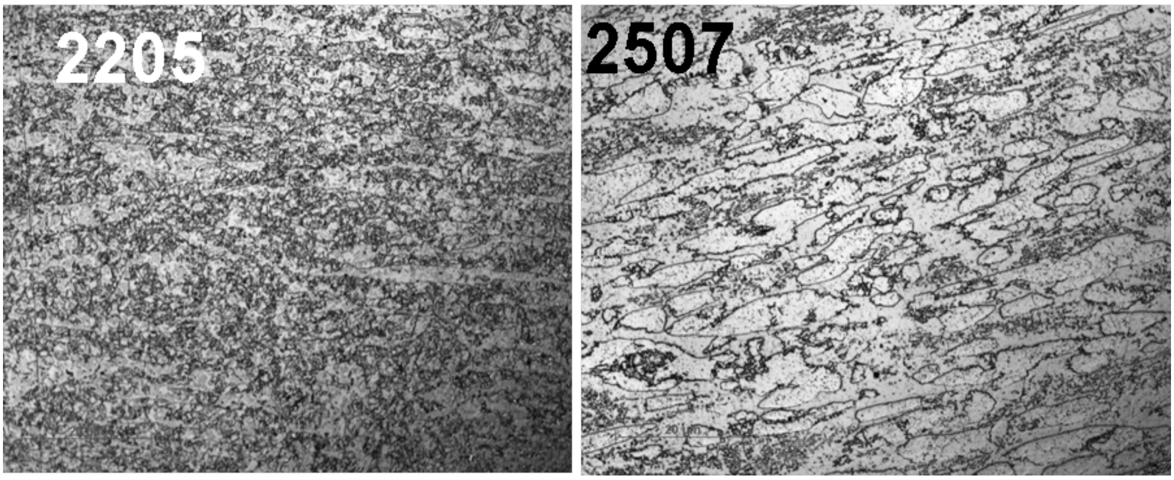

Figure 1 Optical micrographs of the two duplex stainless steels (Magnification x 100)

B. Corrosion Behaviour in 1M Hydrochloric Acid and 1M Sulphuric Acid

The comparative behaviour of the two alloys in 1M hydrochloric acid and 1M sulphuric acid solutions without any additions of inhibitors are summarized in Table 2 to 5 and graphically represented in Fig. 2 and 3.

From the results summarized in Table 2, it is clear that there is a limited beneficial effect of the various plant extracts on the corrosion potential of alloy 2205 in 1 M HCl solution. Statistically only the highest concentration of the Mugwort oil shifted the corrosion potential towards a more noble direction compared to the alloy without any inhibitor in this solution, while one might argue that the highest concentration of the Rosemary oil displayed a similar tendency. In the case of the 2507 alloy, the corrosion potential in almost all cases shifted to a more electronegative potential than that of the alloy without any inhibitor present. Only the highest concentration of Eucalyptus oil had a significantly positive effect in moving the corrosion potential towards more noble values. Not surprisingly, the 2507 alloy had a more electropositive corrosion potential than the 2205 alloy, due to its composition containing more chromium and nickel than that of 2205. In sulphuric acid, only the highest concentration of Jojoba oil shifted the corrosion potential significantly towards a less electronegative value for the 2205 alloy, compared to its corrosion potential when no inhibitor has been added. There is hardly any influence from anyone of the plant extracts on the corrosion potential of 2205 in 1 M of sulphuric acid solution, although the corrosion potential is overall more electropositive than in the hydrochloric acid solution. An identical pattern is observed for the 2507 alloy, although the corrosion potentials tend be more slightly more electropositive in general compared to the 2205 alloy values.

TABLE 2 CORROSION POTENTIAL (CR) FOR 2205 AND 2507 IN 1 M HCl FOR ALL THE INHIBITOS

Inhibitor type	**Concentration (g/l)**	**Ecorr (mV) (± 10)**	
		2205	2507
None	0.0	-347	-277
Honey BG	2.5	-355	-310
	5.0	-341	-308
	10.0	-341	-297
Honey OB	2.5	-351	-312
	5.0	-348	-288
	10.0	-348	-287
Rosemary oil	2.5	-357	-331
	5.0	-359	-312
	10.0	-328	-275
Eucalyptus oil	2.5	-367	-263
	5.0	-362	-276
	10.0	-353	-239
Mugwort oil	2.5	-349	-325
	5.0	-322	-277
	10.0	-311	-258
Jojoba oil	2.5	-354	-313
	5.0	-364	-296
	10.0	-361	-280

TABLE 3 CORROSION POTENTIAL (CR) FOR 2205 AND 2507 IN 1 M H2SO4 FOR ALL THE INHIBITOS

Inhibitor type	**Concentration (g/l)**	**Ecorr (mV) (± 10)**	
		2205	2507
None	0.0	-272	-246
Honey BG	2.5	-283	-247
	5.0	-283	-246
	10.0	-259	-244
Honey OB	2.5	-273	-246
	5.0	-269	-237
	10.0	-265	-245
Rosemary oil	2.5	-276	-251
	5.0	-266	-241
	10.0	-279	-231
Eucalyptus oil	2.5	-267	-247
	5.0	-258	-237
	10.0	-262	-232
Mugwort oil	2.5	-277	-243
	5.0	-275	-242
	10.0	-267	-266
Jojoba oil	2.5	-265	-246
	5.0	-268	-261
	10.0	-227	-218

TABLE 4 CORROSION RATES (CR) FOR 2205 AND 2507 IN 1 M HCl FOR ALL THE INHIBITOS

Inhibitor Type	**Concentration (g/l)**	**CR x 10^2 (± 2 mm/a)**	**% Decrease/ (Increase)**	**CR x 10^2 (± 2 mm/a)**	**% Decrease/ (Increase)**
		2205		2507	
None	0.0	43		14	
Honey BG	2.5	69	(60)	14	0
	5.0	27	37	11	21
	10.0	26	40	14	0
Honey OB	2.5	65	(51)	13	7
	5.0	42	2	5.0	64
	10.0	38	12	8.0	43
Rosemary oil	2.5	52	(21)	16	(14)
	5.0	39	9	6.0	57
	10.0	35	19	4.0	29
Eucalyptus oil	2.5	70	(63)	7.0	50
	5.0	57	(33)	6.0	57
	10.0	42	2	5.0	64
Mugwort oil	2.5	46	(7)	11	21
	5.0	26	40	4.0	29
	10.0	9.0	79	1.0	93
Jojoba oil	2.5	37	14	11	21
	5.0	39	9	10	29
	10.0	30	30	3.0	79

TABLE 5 CORROSION RATES (CR) FOR 2205 AND 2507 IN 1 M H2SO4 FOR ALL THE INHIBITOS

Inhibitor Type	Concentration (g/l)	CR x 10^2 (± 2 mm/a)	% Decrease/ (Increase)	CR x 10^2 (± 2 mm/a)	% Decrease/ (Increase)
		2205		2507	
None	0.0	6.4		4.8	
Honey BG	2.5	15.9	(148)	6.8	(42)
	5.0	15.9	(148)	6.8	(42)
	10.0	3.0	53	3.2	33
Honey OB	2.5	10.0	(56)	7.6	(58)
	5.0	4.8	25	8.5	(77)
	10.0	2.8	56	1.3	73
Rosemary oil	2.5	10.0	(56)	5.0	(4)
	5.0	8.3	30	4.6	4
	10.0	4.1	36	7.0	(46)
Eucalyptus oil	2.5	6.3	2	5.9	(23)
	5.0	5.6	13	3.0	38
	10.0	6.7	(5)	1.6	67
Mugwort oil	2.5	9.1	(42)	5.1	(6)
	5.0	6.2	3	3.0	38
	10.0	7.9	(23)	3.6	25
Jojoba oil	2.5	10.1	(58)	6.5	(35)
	5.0	5.9	8	3.6	25
	10.0	4.6	28	3.7	23

Results revealed that both alloys corrode more in hydrochloric solution than in sulphuric acid medium. In the case of 2205 in hydrochloric acid, it seems as if a too small concentration (amount) of inhibitor increases the corrosion rate rather than retard it. Only once a sufficient amount of inhibitor, usually more than 5 g/l, is present, does it not negatively influence the corrosion rate. Again it seems as only Mugwort oil at its highest concentration exerted a significant influence on the corrosion rate. The largest concentration of Jojoba oil to a lesser extend indicated that it could beneficially influence the corrosion rate, although not substantially. In the case of the 2507 alloy in hydrochloric acid, indications are that all the plant oils investigated, i.e. Rosemary, Eucalyptus, Mugwort and Jojoba, could decrease the corrosion rate if they are present in sufficient (>5 g/l) amounts. Mugwort oil demonstrated the most dramatic effect in inhibiting the corrosion. Overall decreases in corrosion rate varying between 2% and 79% were observed for 2205 in HCl, and between 7% and 93% for 2507 in HCl.

In the sulphuric acid solution, the values for the corrosion rates of alloy 2205 displayed a similar trend than in hydrochloric acid solution, i.e. the addition of the natural products seems to decrease the corrosion resistance at low concentrations before the rates return to those of the parent alloy without inhibitor at the highest amounts added. For both alloys no statistically significant decrease occurred in the corrosion rates with anyone of the plant materials used as inhibitors, although there is an indication in the case of Eucalyptus oil that higher concentrations might yield desirable improvements in the corrosion resistance of alloy 2507 in sulphuric acid. These results in hydrochloric and sulphuric acids are depicted graphically in Figures 2 and 3.

The general observation from the data in Tables 4 and 5 that increasing concentrations of inhibitors above 5 g/l increased their inhibitory action, are in agreement with previous studies on the inhibitory effects of plants extracts.[4,5,8] These inhibition effects could result from an increase in the concentrations of the aromatic organic compounds within the plant extracts that promoted the formation of passivating layers of varying complex organic compounds on the surface of the alloy. It would also be in agreement with the expectation that larger amounts of inhibitor would be able to absorb onto a larger surface area of the alloy and/or form a thicker layer of adsorbed molecules that could retard the corrosion process by coverage of both the anodic and cathodic sites on the surface[16].

According to Hansson *et al.*[17] and Abdel-Gaber *et al.*[18], there is a critical concentration of each inhibitor that optimizes the inhibition efficiency on different alloy in different media, and too little or too much could actually aggravate corrosion rather than reducing it. This correlates well with the observations from the current investigation, where low amounts of inhibitor in especially hydrochloric acid seemed to have increased rather than decrease the corrosion rate of the 2205 alloy. Although the mode of action have not been probed in this investigation, El-Etre *et al*.[5] and Abdel-Gaber *et al.*[18] found that most plant extracts investigated acted as mixed inhibitors.

El-Etre and Abdallah[11] found that natural honey exhibited a very good inhibition performance towards steel corrosion in chloride containing water. However, none of this claimed effect was observed for the duplex stainless steel alloys in the acidic chloride solution investigated. Of all the plant extracts used in this investigation, Mugwort oil shows the most promise for further detailed evaluations. Its inhibitory effect on the corrosion behaviour of the alloys could be the result of an increase in the transfer resistance of the system through the adsorption of mugwort on the alloy surface.[14] According to Benabdellah *et al.*[13], synergistic intermolecular effects of the active molecules of mugwort oil adsorbing on the corroding surface, as well as its cathodic inhibitory effect, which could

modify the hydrogen reduction, are responsible for its efficiency as a corrosion inhibitor.

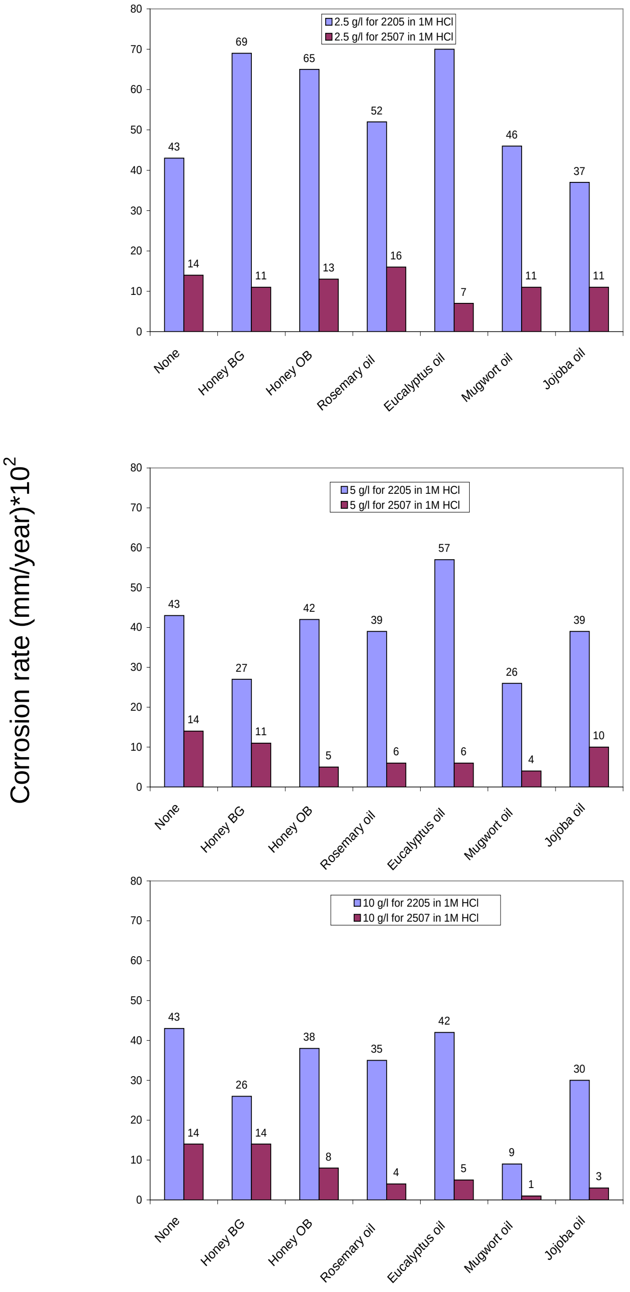

Figure 2 The effect of the inhibitors on corrosion rate of the alloys in 1M HCl

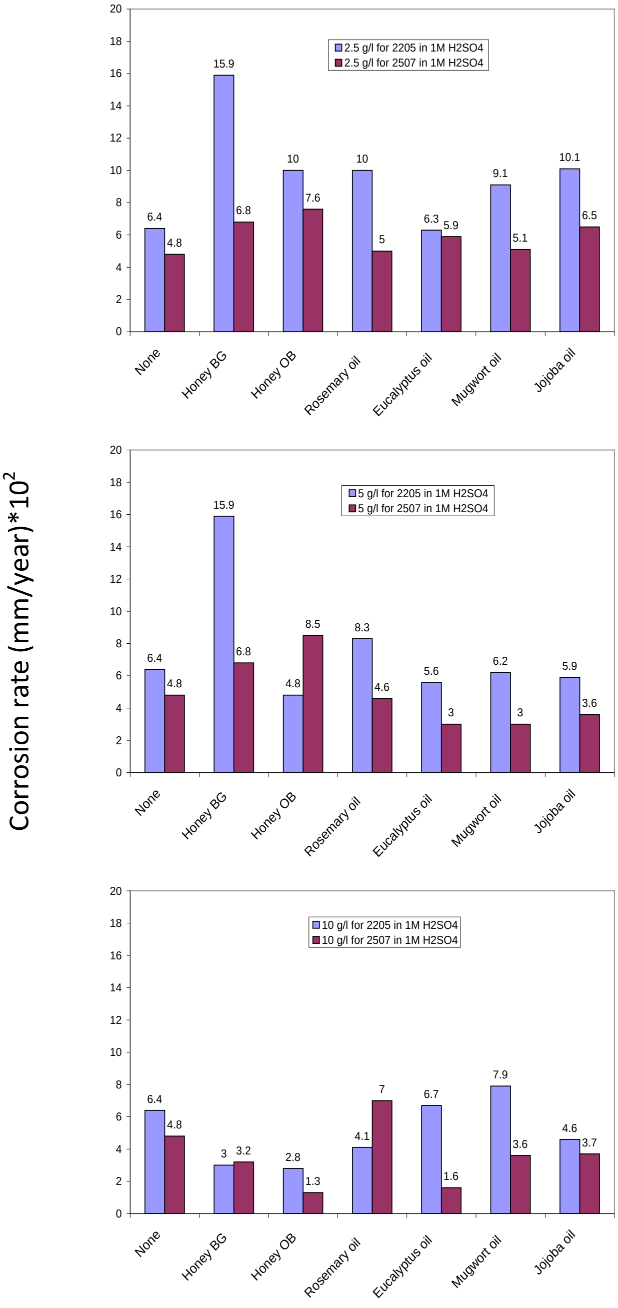

Figure 3 The effect of the inhibitors on corrosion rate of the alloys in 1M H2SO4

IV. CONCLUSIONS

Based on the comparison of the results obtained from this study and the observations made, the following conclusions can be made on effect the different plant extracts on duplex stainless steels

- Both 2205 and 2507 were more resistance to sulphuric acid attack than hydrochloric acid
- Mugwort showed the best potential for inhibiting corrosion, especially in hydrochloric acid, and warrants further detailed investigation.
- Contrary to earlier indications from other studies reported in literature, the inhibitory effect of both honeys proved to be disappointing and worthless on duplex stainless steels in acidic media. This observation indicated that the alloy is an important consideration together with the choice of medium and potential inhibitor to achieve improved corrosion resistance in the system
- The potential plant inhibitors require a rather large minimum critical concentration before displaying any improvement of the corrosion resistance of the duplex alloys.

ACKNOWLEDGEMENTS

The authors wish to acknowledge the financial support received from the DST/NRF Centre of Excellence in Strong Materials of the University of the Witwatersrand,

Johannesburg for this study. The South African Stainless Steel Development Association (SASSDA) is gratefully acknowledged for the supply of the alloys used in the investigation.

REFERENCES

[1] D. A. Jones: Principles and Prevention of Corrosion, Second edition, 1996, Macmillan Publishing Co., USA.

[2] P. B. Raja and M. G. Sethuraman: *Mater. Lett.*, 2008, 62 (1), 113-116.

[3] V.P. Herranz, A.I. Muñoz, J.G. Antón and J.L. Guiñón: *Corr. Sci.*, 2007, 48, 4127–4151.

[4] K.O. Orubite and N.C. Oforka: *Mater. Lett.*, 2004, 58, 1768– 1772.

[5] A.Y. El-Etre, M. Abdallah and Z.E. El-Tantawy: *Corr. Sci.*, 2005, 47, 385–395.

[6] E.E. Oguzie: *Corr. Sci.*, 2007, 49, 1527–1539.

[7] 7(11). A.Y. El-Etre: *Appl. Surf. Sci.*, 2006, 252, 8521–8525.

[8] L.R. Chauhan and G. Gunasekaran: *Corr. Sci.*, 2007, 49, 1143–1161

[9] L. Valek and S. Martinez: *Mater. Lett.*, 2007, 61, 148–151.

[10] A.Y. El-Etre: *Corr. Sci.*, 1998, 39, 1845–1850.

[11] A.Y. El-Etre and M. Abdallah: *Corr. Sci.*, 2000, 42, 731-738.

[12] Y. J. Yee: *Green Inhibitors for Corrosion Control: A Study on the Inhibitive Effects of Extracts of Honey and Rosmarinus Officinalis L. (Rosemary).* M.Sc thesis, University of Manchester Institute of Science and Technology, *Corrosion and Protection Centre*, 2004.

[13] M. Benabdellah, M. Benkaddour, B. Hammouti, M. Bendahhou and A. Aouniti: *Appl. Surf. Sci.*, 2006, 252, 6212–6217.

[14] A. Bouyanzer and B. Hammouti: *Pigment and Resin Techn.*, 2004, 33, 287–292.

[15] K. C. Bendall: Duplex stainless steel in the pulp and paper industry. *Anti-Corr. Meth. and Mater.*, 1997, 44, 170–174.

[16] A.Y. El-Etre: *Corr. Sci.*, 2003, 45, 2485–2495.

[17] C.M. Hansson, L.Mammoliti and B.B. Hope: *Cem. and Concr. Res.*, 1998, 28(12), 1775-1778.

[18] A.M. Abdel-Gaber, B.A. Abd-El-Nabey, I.M. Sidahmed, A.M. El-Zayady and M. Saadawy: Corr. Sci., 2006, 48, 2765–2779.

Herman Potgieter has worked in corrosion for many years, and has held positions at Mintek, Tswane University of Technology, and the University of the Witwatersrand, South Africa, where he was Head of the School of Chemical and Metallurgical Engineering. He is currently a professor at Manchester Metropolitan University, UK, and working on a number of corrosion projects.

P. A. Olubambi hails from Nigeria, where he completed his M.Sc in Metallurgical Engineering at the Akure University of Technology. He graduated from the University of the Witwatersrand with a Ph.D degree in the same field in 2008 before he took up a position as senior lecturer in metallurgy at the Tshwane University of Technology. His current work is focused on the corrosion of sintered stainless steels with PGM additions and tribocorrosion investigations. Dr. Olubambi has published more than 30 papers in peer-reviewed journals, and is currently supervising several postdoctoral, Ph.D and M.Sc students on a number of corrosion projects.

Nompumelelo Thanjekwayo graduated with a B.Sc. Eng. (Metallurgy and Materials Engineering) from the University of the Witwatersrand in 2007, and then enrolled for a M.Sc. degree in Corrosion, which she completed successfully in 2009 at the same institution. In 2010 she joined Kumba Iron Ore as an engineer-in-training at their Sishen mine in the Northern Cape province of South Africa, where she is still employed as a production engineer.